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A review of research on the Kalina cycle

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ABSTRACT

This paper presents a review of the research on the Kalina cycle, including the description of the Kalina cycle, the comparison of the Rankine and Kalina cycle, energy and exergy analysis on the Kalina cycle, different Kalina systems and their different applications. Moreover, different correlations for calculating thermodynamic properties of ammonia–water mixture are screened and discussed. In the end, some technique concerns on ammonia–water mixture, i.e., stability, environmental impacts, safety and corrosion problem etc are also discussed.

Contents

1. Introduction

In thermodynamics, the Carnot cycle has been described as being the most efficient thermal cycle possible, wherein there are no heat losses, and consisting of four reversible processes, two isothermal and two adiabatic. It has also been described as a cycle of expansion and compression of a reversible heat engine that does work with no loss of heat. The century-old Rankine cycle which uses water as working fluid is the real-world approach to the Carnot cycle, and it has been widely used to generate electrical power throughout the world.

Moreover, there are vast amounts of renewable energy sources, such as solar thermal, geothermal, biomass and industrial waste heat. The moderate temperature heat from these sources cannot be converted efficiently to electrical power by conventional power generation methods. Therefore, how to convert these low-grade temperature heat sources into electrical power is of great significance. The Organic Rankine Cycle(ORC) which applies the principle of the steam Rankine cycle, but uses organic working fluids with low boiling points can be used to recover heat from lower temperature heat sources.

In early 1980s Kalina proposed a new family of thermodynamic power cycles using an ammonia–water mixture as the working fluid and this kind of cycle configuration was named Kalina cycle [1–3]. In various novel thermodynamic cycles, the Kalina cycle is the most significant improvement in thermal power plant design since the

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Nomenclature

wt	Weight [–]
p	Pressure [kPa],[MPa]
T	Temperature [K],[°C]

Greek symbol

η	Efficiency[–]

Subscripts

L	Low
M	Medium
ti	Turbine inlet

Abbreviations

ORC	Organic Rankine cycle
KCS	Kalina Cycle System
EOS	Equation of State
RKC	Rankine–Kalina Combined
PR	Peng–Robinson
WHR	Waste heat recovery
OTEC	Ocean thermal energy conversion
HRVG	Heat recovery vapor generator
VLE	Vapor liquid equilibrium
HE	Heat exchanger
LT	Low temperature
HT	High temperature
LPC	Low pressure condenser
HPC	High pressure condenser
DCSS	Distillation and condensation sub system.

advent of the Rankine cycle in the mid 1800s and it has been considered as an ambitious competitor against the Organic Rankine Cycle.

This review focuses on the research achievement in the Kalina cycle. This paper has reviewed comparisons between the Rankine and Kalina cycle in literature. Based on the first and second law of thermodynamics, the Kalina cycle has been energy and exergy extensively analyzed. Different Kalina systems and their different applications were briefly discussed in this review. As the working fluid, ammonia–water mixture plays a key role in the Kalina cycle. Therefore, different correlations for calculating thermodynamic properties of ammonia–water mixture are screened and discussed in this review. In the last section, some technique concerns on ammonia–water mixture for engineering application of the Kalina cycle, i.e., stability, environmental impacts, safety and corrosion problem etc are also discussed.

2. Description of the Kalina cycle and comparison between the Rankine and Kalina cycle

2.1. Description of the Kalina cycle

In order to replace the previously used Rankine Cycle as a bottoming cycle for a combined-cycle energy system as well as for generating electricity using low-temperature heat resources, Alexander I. Kalina designed a new power cycle in which ammonia–water is used as a working fluid [3].

The first version of the Kalina cycle is characterized by a second condenser, after the separator, at one intermediate pressure, allowing an additional degree of freedom in the composition of the boiling mixture and allowing the distillation unit to operate at a pressure lower than the maximum one. A further difference concerns the recuperative heat exchanger, which, in the Kalina scheme is placed downstream the turbine. In these situations (medium-low temperatures heat sources application and small power conversion system) the plant layout may be simplified and the cycle has a single main condenser, at the lowest cycle temperature, and the separator is placed after the evaporator [4].

A simplified Kalina cycle which has been analyzed by many researchers [5,6] is adopted in this review to demonstrate concept of the Kalina cycle and its flow diagram is depicted as Fig. 1. (The number with square bracket stands for a device in the cycle, while the number without a bracket stands for a state point in the cycle.) As Fig. 1 shows, this is a bottoming cycle fed by exhaust gases (1, 2) to the boiler. Superheated ammonia–water vapor (3) is expanded in a turbine to generate work (4). The turbine exhaust (5) is cooled (6, 7, 8), diluted with ammonia-poor liquid (9, 10) and condensed (11) in the absorber by cooling water (12, 13). The saturated liquid leaving the absorber is compressed (14) to an intermediate pressure and heated (15, 16, 17, 18). The saturated mixture is separated into an ammonia-poor liquid (19) which is cooled (20, 21) and depressurized in a throttle and ammonia-rich vapor (22) is cooled (23) and some of the original condensate (24) is added to the nearly pure ammonia vapor to obtain an ammonia concentration of about 70% in the working fluid (25). The mixture is then cooled (26), condensed (27) by cooling water (28, 29), compressed (30), and sent to the boiler via regenerative feed water heater (31).

The conspicuous efficiency advantage characteristic of the Kalina cycle is realized from the heat exchange processes of the heat acquisition in the evaporator and the heat rejection in the condenser. Additional efficiency is achieved by the recuperator exchangers. These gains are made possible by the unique "variable" boiling and condensing characteristic of the ammonia–water mixture working fluid. The varying temperature during the heat-transfer processes reduces the thermodynamic irreversibility of heat exchange and the effect of the thermal pinch in the boiler.

When ammonia–water mixture is heated, the more volatile ammonia tends to vaporize first than pure water. As the ammonia concentration of the remaining liquid decreases, saturation temperature rises, providing a better match to a hot gas heat source such as a gas turbine exhaust than the constant-temperature evaporation of a pure substance (water/steam). The working fluid is split into streams with different concentrations, providing a great deal of flexibility with which to optimize heat recovery and allowing condensation at a pressure greater than atmospheric.

2.2. Comparison between the Rankine/ORC and Kalina cycle

The Kalina cycle is principally a "modified" Rankine cycle. The modifications that complete the transformation of the cycle from Rankine to Kalina consist of proprietary system designs that specifically exploit the virtues of the ammonia–water working fluid. These special designs, either applied individually or integrated together in a number of different combinations, comprise a family of unique Kalina Cycle Systems. This is somewhat analogous to the Rankine cycle which, in fact, has many design options such as reheat, regenerative heating, supercritical pressure, dual

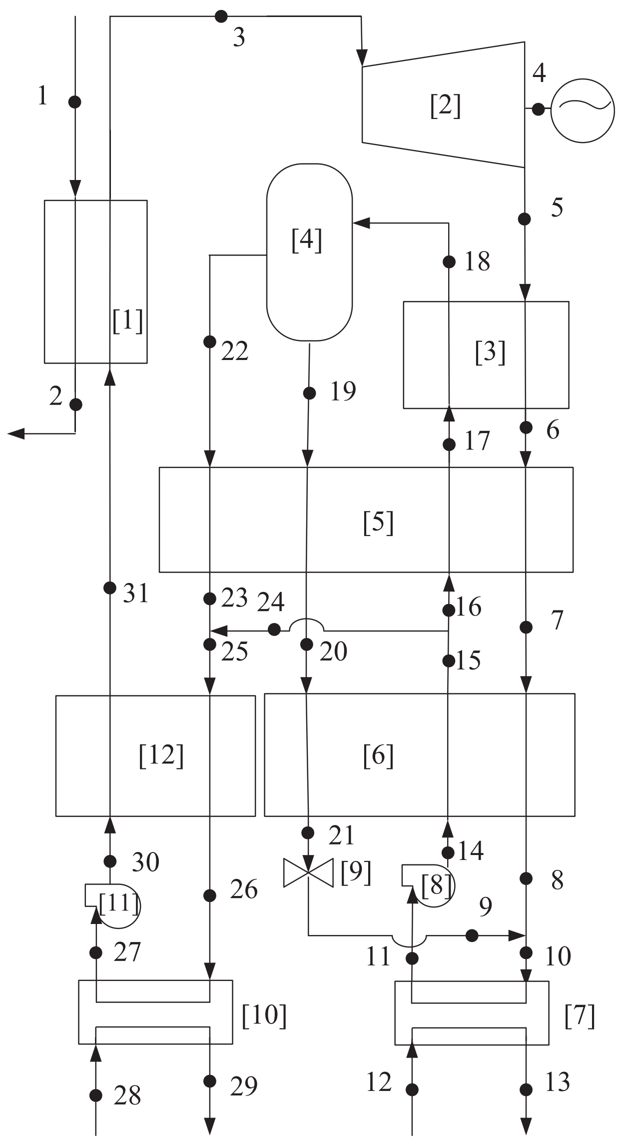

Fig. 1. A simplified Kalina cycle [5,6].
Note: [1] boiler; [2] turbine; [3] distiller; [4] separator; [5] reheater #1; [6] reheater #2; [7] absorber; [8] condensate pump; [9] throttle; [10] condenser; [11] boiler feed pump; [12] feed water heater.

pressure, etc. all of which can be applied in a number of different combinations in a particular plant [7,8].

In theory, the Kalina cycle can help convert approximately 45% of a direct-fired system's heat input to electricity and up to 52% for a combined-cycle plant (a gas turbine produces exhaust, which enables a steam turbine to produce electricity). This compares with about 35% and 44%, respectively, for the steam cycle [9]. Moreover, the Kalina cycle cycles can give up to 32% more power in the industrial waste heat application compared to a conventional Rankine steam cycle. However, the Kalina cycle in small direct-fired biomass-fueled cogeneration plants do not show better performance than a conventional Rankine steam cycle [10]. When both cycles are used as a "bottoming" cycle with the same thermal boundary conditions, it can be found when the heat source is below 1100 °F(537 °C), the Kalina cycle may show 10 to 20% higher second law efficiencies than the simple Rankine cycle [5].

Jonsson [11] in her doctorial thesis investigated the Kalina cycles as bottoming processes for natural gas–fired gas and gas–diesel engines. It was shown that the Kalina cycle has a better thermodynamic performance than the steam Rankine cycle for this application. All simulated Kalina cycle configurations generated more power than the steam cycles, except for one simple Kalina cycle configuration compared with a dual-pressure steam cycle. The best Kalina bottoming cycle could generate 40–50% more power than a single-pressure steam cycle and 20–24% more power than a dual-pressure steam cycle. A Kalina bottoming cycle could add 6–8 percentage points in efficiency to the gas engines, while a single-pressure steam bottoming cycle could add about 5 percentage points. For the gas–diesel engines, the efficiency augmentation was 4–7 percentage points for the Kalina bottoming cycles, 4–5 percentage points for a single-pressure steam cycle and 4–6 percentage points for a dual-pressure steam cycle.

The adoption of the Kalina cycle to a certain heat source and a certain cooling fluid sink has one degree of freedom more than the ORC cycle, as the ammonia–water composition can be adjusted as well as the system high and low pressure levels [12]. In order to obtain high thermodynamic performances, the Kalina cycle requires a very high maximum pressure (for instance, 100 bar for the Kalina cycle against about 10 bar for the ORC cycle [4]). Therefore, comparing with an ORC, the Kalina Cycle System 11 [8,13] (KCS11) has better overall performance at moderate pressures for low-temperature geothermal heat sources [14].

Taking temperature range into consideration, Lu et al. [15] assessed a combination of the high heat transfer efficiency of the heat source and the low heat losses to the heat sink gives the Kalina cycle a much higher overall efficiency than the Organic Rankine Cycle within the same temperature range. However, the adoption of Kalina cycle, at least for low power level and medium-high temperature thermal sources, seems not to be justified because the gain in performance with respect to a properly optimized ORC is very small and must be obtained with a complicated plant scheme, large surface heat exchangers and particular high pressure resistant and no-corrosion materials. Therefore, the more believable application of the Kalina cycle is restricted to medium–low temperatures heat sources (typical maximum temperatures of 300–400 °C in the case of heat recovery, and 100–120 °C in the binary geothermal plants) and to small power conversion systems [4,14,16–19].

Comparison performed in literature [20] for similar temperatures (108–122 °C) shows actual increase of 3% for the Kalina cycle over the ORC, and not 30–50% as referenced in literature [13]. Moreover, in a particular case in the Republic of Croatia, the geothermal source has a higher temperature(175 °C), therefore, ORC in which isopentane is used as the working fluid has better both the thermal efficiency (the First Law efficiency) and the exergetic efficiency (the Second Law efficiency): 14.1% vs. 10.6% and 52% vs. 44% [19].

3. Energy and exergy analysis on the Kalina cycle

Compared with the Rankine cycle, the Kalina cycle is a novel thermodynamic cycle. Therefore, the conclusion drawn from both energy and exergy analysis on the Kalina cycle is crucial for its further practical application.

3.1. Energy analysis based on the first law of thermodynamics

Compared with the Rankine cycle, the Kalina cycle has similar devices in cycle configuration. However, the Kalina cycle has one degree of freedom more than the Rankine cycle which is the fraction of ammonia–water mixture. Therefore the thermodynamic performance of the Kalina cycle will be greatly affected by the fraction of ammonia–water mixture and the parameters of devices in the cycle.

With regard to the fraction of ammonia–water mixture, design studies of Kalina cycle for geothermal resources with low to moderate temperature indicate different compositions of ammonia–water mixtures, commonly about 70 wt% ammonia [12,13,21–23]. Marston [24] holds the similar opinion in his research on a three-stage Kalina cycle and concluded the Kalina cycle models have frequently used a boiler working fluid of 70 wt% ammonia; however, the optimum composition is a function of many design parameters. Nag and Gupta [25], in their exergy-based study, determined that the most effective ammonia fraction is about 73 wt%. A similar exergy-based analysis by Borgert and Velasquez [26] put the optimum ammonia fraction at about 58 wt%. Nasruddin [27] et al. performed an energy and exergy analysis on KCS34 with mass fraction ammonia–water mixture variation. The result of their study shows that the maximum efficiency and power output are achieved at 78 wt% ammonia–water mixture. Arslan [28] performed an exergoeconomic evaluation assuming KCS 34 was used for generating electricity from Simav geothermal field and found that for the case with 80 wt% ammonia fraction, the maximum energetic efficiency is 14.9%. The only available application of KCS34 is in Husavik, Iceland, with an installed capacity of 2 MW and a working fluid of 82 wt% ammonia [20]. When the Kalina cycle is matched with the Rankine cycle to establish a combined cycle, the optimum fraction of ammonia water mixture was found to be 89 wt% [29].

With respect to the first law efficiency, among all devices in the Kalina cycle, the key parameters which can influence the cycle performance are: separator temperature [24,25,30–32], turbine inlet pressure [14,29,33–35], turbine inlet temperature [25,32,34,35], and turbine output pressure [27,35]. Turbine inlet condition (temperature and composition) and separator temperature can effect both the first and the second law efficiencies of the Kalina cycle [25].

For a given turbine–inlet mass fraction, as the separator temperature increases, the cycle efficiency increases up to a maximum and then starts to decrease. For a given turbine–inlet mass fraction and separator temperature, the cycle efficiency will be increased by decreasing the separator pressure. At constant turbine inlet temperature, the separator temperature decreases with the increase in the turbine inlet concentration [32]. Moreover, for a given separator temperature, the cycle efficiency will be increased by decreasing the separator pressure [31].

By increasing the pressure and the temperature at the inlet of turbine and decreasing the back pressure of turbine, the cycle thermal efficiency can be obviously increased [35]. For a Rankine–Kalina Combined (RKC) cycle, its efficiency depends on the turbine inlet pressure (Bottoming cycle). In the RKC cycle, maximum output is obtained at turbine inlet pressure of 41.70 bar [29]. Moreover, research shows that for a given turbine inlet pressure, an optimum ammonia fraction can be found that yields the maximum cycle efficiency [14].

If the outlet pressure from turbine is constant, by increasing the ammonia mass fraction the system efficiency will increase. If the mass fraction is constant, by decreasing exit pressure from turbine, it will increase the system efficiency [27].

According to the research of Rogdakis [36], the efficiency of the Kalina cycle in terms of the two pressures p_M (medium pressure) and p_L (low pressure) may be calculated as

$$\eta = \frac{A}{p_L} + Bp_L + C \tag{1}$$

where,

$$A = -0.94470085p_M^2 + 8.8705682p_M - 22.047349 \tag{2}$$

$$B = -0.38132389p_M^2 + 4.0481463p_M - 11.702681 \tag{3}$$

$$C = 1.2152930p_M^2 - 13.127963p_M + 81.367228 \tag{4}$$

Lolos and Rogdakis [37] calculated the efficiency η for a great number of combinations of the minimum temperature T_L (12 to 22 °C) and low pressure p_L (1 to 4 bar) and derived the following correlations linking the efficiency with independent variables of the cycle(T_L, the minimum temperature; p_L, the low pressure, t_H, the maximum temperature of the cycle).

$$\eta = a_2 + b_2T_H + c_2T_H^2 \tag{5}$$

where,

$$a_2 = -0.049 - 0.0022T_L \tag{6}$$

$$b_2 = 0.0035 \times 0.92^{1/p_L} \tag{7}$$

$$c_2 = -2.36 \times 10^{-6} - 2.19 \times 10^{-6}p_L + 3.14 \times 10^{-7}p_L^2 \tag{8}$$

3.2. Exergy analysis based on the second law of thermodynamics

The first law of thermodynamics, often referred to as the law of conservation of energy, deals with nothing more than the "accounting" of energy. In a power cycle, the heat input to the system is equal to the sum of work and any waste heat produced or discharged during the process.

However, in order to analyze a power cycle, besides "how much" told by the first law of thermodynamics, we also want to know "why". Why are the losses what they are? Moreover how to reduce these losses? The answers to these questions are crucial for understanding of a more efficient cycle and the second law of thermodynamics can give us these answers. The second law of thermodynamics basically says that "work" will, or can be done by an energy medium(working fluid) as it goes from a high temperature to a low temperature inside a heat engine such as a turbine. After producing work in the turbine, working fluid will have to give up its remaining heat to the heat sink via a heat exchanger.

A basic parameter in sizing heat exchangers is called pinch point. This is simply the minimum temperature difference or temperature driving force between fluids. Pinch point is reached where it becomes cost prohibitive to further reduce the temperature difference between the two fluids in heat transfer process.

Taking the Rankine cycle for instance, in the Rankine cycle more than half of the heat transfer occurs during the boiling process. Both pressure and temperature are constant during boiling; the gas at the pinch point, where the water starts to boil, must be at a higher temperature than the boiling water. The pinch point is a limitation on power output because: (1) It can force a higher than otherwise necessary heat sink temperature. (2) The gas at the point where vaporization is complete will be at a much higher temperature than the steam and the large temperature difference results in a loss of availability.

The Kalina cycle utilizes a mixture of ammonia and water as the working fluid. When the liquid mixture is heated, the more volatile ammonia tends to vaporize first than does pure water. The temperature of the remaining saturated liquid rises as the ammonia concentration decreases. Thus a better match to the temperature change of the gas is obtained and the potential exists for significant increases in cycle efficiency.

El-Sayed and Tribus [5] gave a detailed analysis of the entropy generations for the Rankine and Kalina cycle on the following boundary conditions. The turbine exhaust temperature is taken to the 1000 °F (537 °C). The flow is taken to be 100,000 lb/hr. The cooling "sink" is taken at 55 °F (12.7 °C). The results show only 75.1% of the input exergy can be transmitted to the rest of the Rankine cycle. In the Kalina cycle 85.1% of the original exergy will be available to the rest of the cycle.

Wall et al. [6] applied the energy-utilization diagram, a graphic method to describe the exergy losses in industrial processes, to a 3 MW Kalina bottoming cycle to perform an exergy study. The energy-utilization diagram of the Kalina cycle is very tight. That means the cycle is very well optimized.

With respect to the second law efficiency, the ammonia mass concentration at turbine inlet (x_{ti}) is a key parameter for optimizing the Kalina cycle so that the exergy loss of the cycle is minimum. At low values of x_{ti}, the turbine loss is high and decreases with increasing x_{ti}, whereas, the heat recovery vapor generator irreversibility is low for low values of x_{ti} and increases with increase of x_{ti}. As a result, the second law efficiency increases first and then decreases with x_{ti}. There is an optimum value of x_{ti}, where the second law efficiency is maximum and it is different for the different values of the turbine inlet temperature and the separator temperature [25].

Among all devices in the Kalina cycle, the boiler(heat recovery vapor generator) has the maximum exergy destruction. The second and third largest exergy destruction occurs in turbine and condenser, respectively. The exergy destruction in high temperature recuperator and that in low temperature recuperator account for the other main exergy destruction [6,29,38–40]. Therefore, reducing the exergy losses of these components especially the boiler can distinctly improve the cycle performance. Moreover, as a critical component for a high pressure Kalina cycle, turbine must be either multistage or rotate at very high rotational speed in order to guarantee satisfying isoentropic efficiencies [4].

4. Different Kalina systems and their different applications

The prototype of the Kalina cycle was proposed in early 1980s [1–3]. The cycle published in 1984 [3] was later designated as Kalina Cycle System 1(KCS 1). In order to attain a significant improvement in matching of the working fluid and the heat-source heat-temperature curves in the boiler, a new, improved variant which provides a 10% efficiency improvement over the initial KCS 1, has been developed and was designated as KCS 6. KCS 1 would be preferable for small units (below 20 MW total output; about an 8 MW bottoming cycle), while the more complicated KCS 6 would be preferable for larger units [41].

Generally speaking, each Kalina Cycle System in the family of designs has a specific application and is identified by a unique system number. Table 1 [7] lists the Kalina cycle developmental status up to the end of 1980s.

KCS 6, intended as the bottoming cycle for a gas turbine based combined cycle, provides the highest efficiency of all the Kalina cycles [7,8]. KCS 5 is particularly applicable to direct(fuel) fired plants [8]. KCS 5n is similar to KCS 5, except the water loop has been removed. Because the incoming gases are not at as high temperature as in a combustion system, there is not as much heat available at the high end of the system. As in KSC 5, the hot gases are used primarily for superheating and not for boiling [7]. KCS 2 is intended for the applications where the sources are generally below 375 °F [7].

One of the most important applications of the Kalina cycle is power generation from low temperature geothermal [14,15,17,20,23,27,28,45,46]. Kalina cycle geothermal plants offer significant efficiency, cost, safety and environmental advantages over geothermal binary power plants using Organic Rankine Cycle(ORC) technology. A Kalina plant generates 30 to 50% more power than an ORC plant [13].

There are many different Kalina system designs for geothermal applications. Fig. 2 shows three of the more basic Kalina Cycle Systems (KCS) designs for low temperature geothermal. KCS 11 is most applicable for geothermal temperatures from about 250 to 400 °F [121 to 204 °C]. KCS 34 and KCS 34g are suitable for temperatures below 250 °F [121 °C]. For these lower temperature systems, KCS 34 is more suitable for combined power production and downstream district heating applications, while KCS 34 g is suited for smaller size plants [13].

If the heat source had a maximum temperature of only 240 °F (116 °C), the ammonia–water vaporization process would stop at a point where liquid still present in the process stream. This is the reason separators are shown in Fig. 2 for KCS 34 and KCS 34g systems used on lower temperature geothermal applications. The separator ensures that only the vapor directed to the turbine. KCS 11 and 34 designs have recuperators in the turbine exhaust stream prior to the condenser. Note that KCS 34g has no provisions for recuperating the turbine exhaust energy. This design is especially suited for small unit applications that can cool the geothermal heat (or waste heat) source down to a low temperature without scaling problems [13].

The temperature of the heat sources(preheater and clinker cooler exhaust streams) for a typical cement facility are in the range, 200 °C to 400 °C. Both of these heat sources are classified as medium to low temperature heat for electrical power generation. These heat streams are well matched for use of the Kalina cycle

Table 1
Kalina cycle developmental status [7].

System number	Application	Cycle efficiency ratio (Kalina/Rankine)	Net plant output ratio (Kalina/Rankine)	Development status
1	Bottoming cycle small plants	(32.0/26.6)=1.2 [43]	(49.5/46.0)=1.07 [a]	Design completed for Canoga Park Demonstration
2	Low temperature geothermal	(20.5/13.1)=1.56 [a]	(17.6/10.3)=1.71 [b,c]	Design completed
3	High temperature geothermal and industrial waste			Under development
4	Cogeneration			Planned
5	Direct-fired for coal and other solid fuels	(48.6/42.2)=1.15 [42]	(40.9/34.6)=1.18 [d]	Design completed
5n	High temperature gas-cooled nuclear reactor	(46.0/36.0)=1.28 [43]	(46.0/36.0)=1.28 [44]	Design completed
6	Bottoming for utility combined cycle	(37.8/28.7)=1.32 [42]	(56.4/51.0)=1.11 [a]	Design completed
7	Direct fired, split cycle	(50.0/42.2)=1.19 [42]	(42.4/34.6)=1.22 [d]	Under development
8	Bottoming cycle, split cycle	(39.0/28.7)=1.36 [42]	(56.67/51.0)=1.11 [a]	Under development
9	Retrofit subsystem for existing plant	N/A	(40.4/34.6)=1.17 [d]	Under development
12	Low temperature geothermal	(19.2/13.1)=1.47 [44]	(16.5/10.3)=1.6 [b,c]	Design completed

[a] For entire combined cycle.
[b] Compared to Heber Plant binary cycle.
[c] Includes losses due to reinjection pumps and other auxiliaries.
[d] Includes losses from fuel handling and plant auxiliaries.

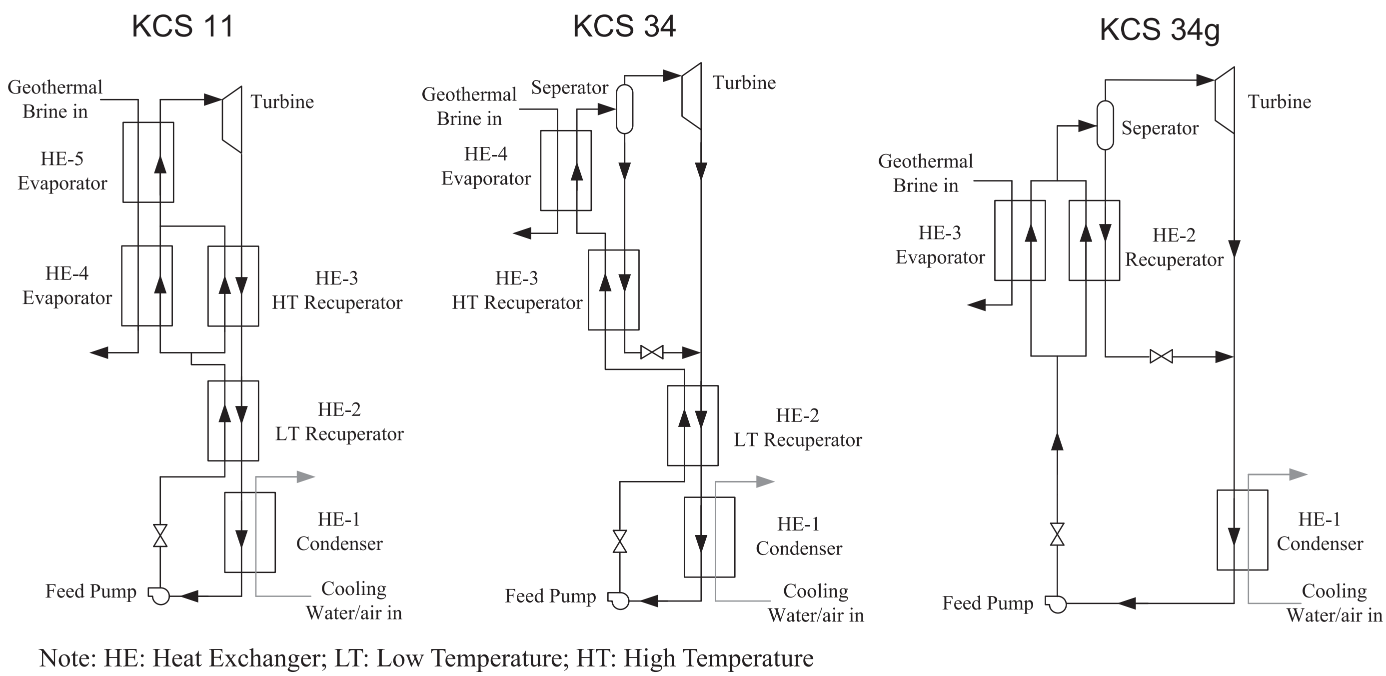

Fig. 2. Kalina Cycle Systems for Low Temperature Geothermal.

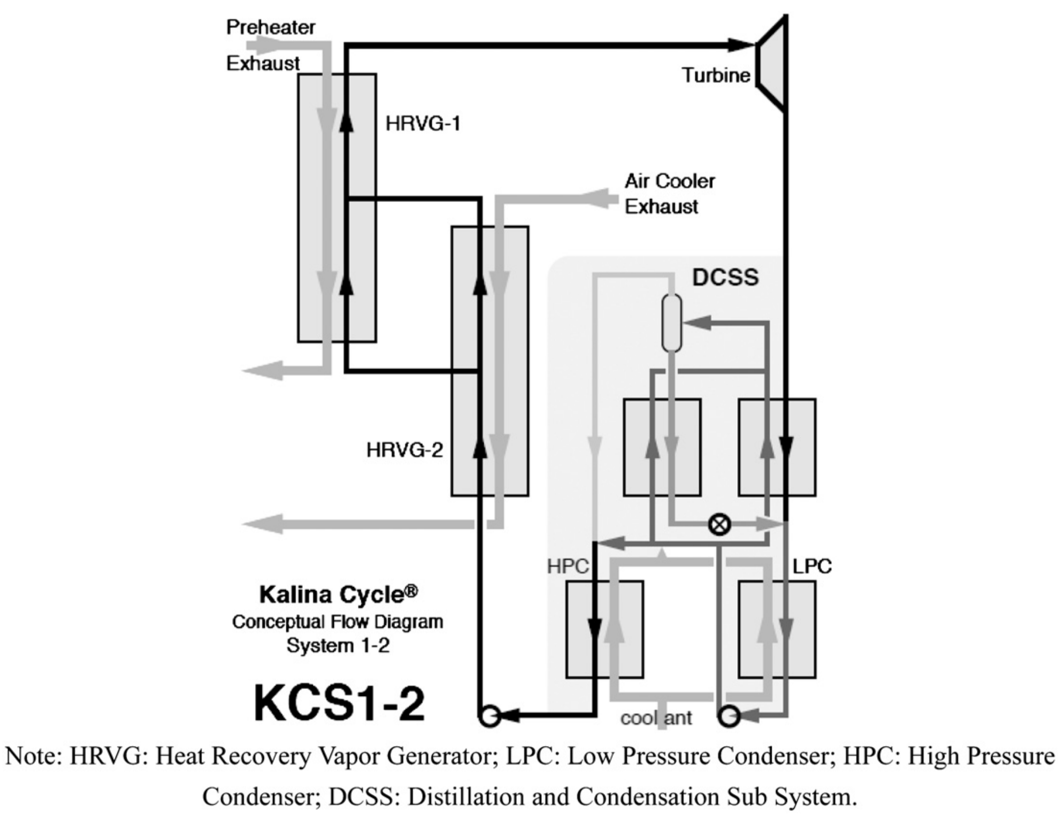

Fig. 3. Typical Kalina Cycle for a Cement Klin.

process for waste heat recovery (WHR) to produce electricity [47,48]. The Kalina cycle can use the waste heat from the cement production process to generate electrical energy with no additional fuel consumption, and reduce the cost of electric energy for cement production.

Kalina Cycle System(KCS) 1–2 is adopted for a waste heat recovery power plant for a cement facility [47]. Its typical process schematic is shown in Fig. 3. Wang et al. [49] used single flash steam cycle, dual-pressure steam cycle, Organic Rankine Cycle (ORC) and the Kalina cycle for cogeneration to recover waste heat

from the preheater exhaust and clinker cooler exhaust gases in cement plant. Compared with other systems, the Kalina cycle can achieve the best performance from the view point of exergy efficiency. The ORC shows the lowest exergy efficiency under the same condition, while single flash steam cycle and dual-pressure steam cycle have a better performance in recovering waste heats of cement plant. It is inferred that the ORC, which is superior in recovering low-grade waste heat, may be not suitable for waste heat recovery in cement plant, due to relatively high temperature of waste heat sources. With this temperature range, the Kalina cycle is 20% to 40% more efficient than the Rankine cycle [47].

Besides the applications in geothermal and cement industry and the application introduced at the beginning of this section, other application of the Kalina cycle has also been developed for ocean thermal energy conversion(OTEC) [34], gas turbine [7,8] or diesel engine based combined cycle [4,16,50], solar [51–53], coal-fired [8] and even nuclear.

5. Working fluid properties

The lifeblood of the Kalina cycle is an ammonia–water mixture working fluid. Ammonia–water mixtures have many basic features unlike that of either pure water or pure ammonia. A mixture of the two fluids behaves like a totally new fluid. There are four primary differences [8].

First, an ammonia–water mixture has a varying boiling and condensing temperature. Conversely, both pure water and pure ammonia have constant boiling and condensing temperatures.

Second, the thermophysical properties of an ammonia–water mixture can be altered by changing the ammonia concentration. The thermophysical properties of water and ammonia are fixed.

Third, ammonia–water has thermophysical property that causes mixed fluid temperatures to increase or decrease without a change in the heat content. The temperature of water or ammonia does not change without a change in energy.

The final difference is not really a change in a basic feature, but rather an important change in a fluid property. This is the freeze temperature. Water freezes at a relatively high temperature of 0 °C, while pure ammonia freezes at −78 °C. Solutions of ammonia–water have very low freezing temperatures.

The use of ammonia in the mixture permits efficient use of waste heat streams, allowing boiling of the ammonia–water working fluid to start at lower temperatures. The use of a binary fluid allows the composition of the working fluid to be varied through the use of distillation, providing a richer concentration in the heat-acquisition stage heat recovery vapor generator (HRVG) and leaner composition in the low-pressure condenser. Since the molecular weight of ammonia is close to that of water, a standard back-pressure, multistage turbine-generator is used.

A mixture of ammonia and water is used as a working fluid for several reasons [33,47,48]:

First, the use of a lighter component (ammonia), allows efficient use of the waste heat stream at a higher pressure by causing boiling to start at lower temperature.

Second, the use of a mixture allows the composition to be varied through the use of distillation, resulting in a richer composition for the boiler, and a leaner composition in the low-pressure condenser. The variable temperature boiling process of ammonia–water reduces losses in heat transfer processes throughout the power plant, thereby increasing the efficiency of the power cycle.

Third, because of the similar molecular weights of ammonia and water (17.03 vs. 18.015) the ammonia–water vapor behaves virtually the same as steam, which allows the use of standard steam turbine components.

Fourth, standard materials can be used. Carbon steel and standard high-temperature alloys are acceptable for handling ammonia. Only the use of copper and copper alloys is prohibited in ammonia service.

Fifth, ammonia is readily available and relatively inexpensive.

Sixth, ammonia is not harmful to the environment.

Seventh, there are proven safety procedures for the handling and use of ammonia in industrial plant applications.

By contrast, the hydrocarbons heretofore dominant in this application are flammable and may represent an explosion hazard. Organic fluids are also identified as contributors to photochemical smogs, depletion of the ozone layer. In the event of an accidental spill, organic fluids can pose a hazard to local ecosystems.

Thermodynamic performance analysis of the Kalina cycle requires thermophysical property data for ammonia–water mixtures, for which composition (expressed as mass fraction of ammonia in the mixtures) represents a third independent variable.

With the introduction and development of the Kalina cycle technology, Exergy Inc. which was founded by A. I. Kalina began to perform the research on ammonia–water properties. In 1998, Exergy Inc. completed its first set of ammonia–water properties by combining the experimental data of numerous researchers with a theoretical approach by Kalina, Tribus and others. This work is embodied in a computer program called "WATAM" which Exergy Inc. utilizes in the design of all its Kalina Cycle power plant designs [54]. Compare WATAM with Peng–Robinson(PR) Equation of State (EOS) in modeling the high-pressure ammonia–water system for the Kalina cycle study, it can be found although the PR EOS provided a reasonable fit of the vapor liquid equilibrium(VLE), it tended to overestimate the ammonia concentration in the near-critical vapor phase. The PR EOS also overestimated mixture critical pressures. WATAM provided a slightly more accurate description of the VLE, especially in the near-critical region. WATAM also yielded a much better correlation of saturated liquid densities for the ammonia–water mixture than the PR EOS [55].

More than 40 correlations developed by different researchers for thermodynamic properties of ammonia–water mixture are found in literature [25,55–98]. The theoretical background and basis of these correlations can be divided into nine groups: cubic equations of state [56–69], virial equations of state [68,70–72], Gibbs excess energy [25,55,59,62,65,67–69,71–86], corresponding states method [87–92], perturbation theory [85,93], group contribution theory [64,94], Leung-Griffiths model [95], Helmoltz free energy [96] and polynomial functions [97,98].

Most of the correlations for the thermodynamic properties of ammonia–water mixtures available today have been developed for lower temperatures and lower pressures than common in power cycles. When used in simulations of a simple Kalina cycle, some correlations previously used in ammonia–water power cycle simulations, give cycle efficiencies with a difference not larger than 3%. The differences in saturation properties between the correlations are, however, considerable at high pressures, high temperatures and high mass fractions of ammonia. Even though the new correlation seems to be more theoretically reasonable than the older correlations previously used in power cycle simulations, the differences in the final results of the thermal efficiency cycle simulations are still small. The conclusions made in earlier studies using the older correlations should therefore be reasonable. However, it should be pointed out that no, or very little, experimental data is available in the critical and supercritical region of the ammonia–water mixtures and that the

behavior of the mixture in this region is therefore uncertain [10,99,100].

6. Technique concerns for engineering application of the Kalina cycle

The main concern for engineering application of the Kalina cycle focuses on the environmental and safety features of ammonia–water mixture.

While someone may believe the strong odor and irritating properties of ammonia are a nuisance, these are actually beneficial. First, they are self-alarming. Second, these properties will insure that operators maintain a good tight plant.

Ammonia is produced as a decomposing byproduct of nature. It is part of nature, and therefore does not contribute to global pollution or global warming. Ammonia has even been reported to benefit the environment by neutralizing acidic pollutants in the air.

Fire and explosion hazards due to ammonia are very low. Ammonia will not support combustion after the ignition source is withdrawn.

And finally, ammonia is gaseous at atmospheric pressure. It is much lighter than air and, therefore, easy to vent off [101].

Another concern is the chemical stability of ammonia–water mixture and the potential corrosion problems of device caused by ammonia–water.

Tests have been conducted to evaluate the impact of an ammonia–water environment on the life expectancy of traditional power plant materials. Testing has been conducted both in the laboratory and in the Canoga Park demonstration plant over the past 20 years. The results of the tests indicate that for power plants which will operate up to turbine throttle temperatures of 1000 °F, traditional materials of construction for power plants are acceptable [54]. However, using ammonia–water mixture at more than 400 °C is not advisable, because at higher temperature NH_3 becomes unstable which leads to nitride corrosion [29].

The ammonia–water working fluid in a Kalina cycle plant presents different material issues than in a steam plant. Oxidation of plant components throughout the power cycle is less likely because oxygen levels within the working fluid are extremely low. However, nitridation of high temperature components is a concern which should be considered when selecting superheater, reheater and high temperature turbine parts [46]. Except for the turbines and superheaters, the temperatures are low enough that carbon steels may be used [7]. As for the turbine design, copper-based alloys are subject to corrosion in the presence of ammonia, so some material substitution may be necessary [30].

In 2009, Whittaker [102] made a detail investigation into corrosion problems at the Kalina cycle geothermal power plant in Husavik, Iceland. The investigation asserts mild steel and aluminum seem to be inappropriate materials for Kalina Cycle Systems but several stainless steels (304, 316, nitronic 60 and duplex) as well as 6Al–4V titanium do not appear to suffer from corrosion.

7. Conclusion

The research on the Kalina cycle was reviewed. The Kalina cycle was developed in order to replace the previously used Rankine Cycle as a bottoming cycle for a combined-cycle energy system as well as for generating electricity using low-temperature heat resources. Generally speaking, the Kalina cycle has a better thermodynamic performance than the Rankine cycle and organic Rankine cycle with respect to both energy and exergy efficiency.

The Kalina cycle has a family of configurations used in different fields. Electricity generation from geothermal is the only successful application of the Kalina cycle so far. Different correlations based on nine groups of different theoretical background can be used for calculating thermodynamic properties of ammonia–water mixture and cycle performance analysis. Ammonia–water mixture is environmentally friendly and safe enough for engineering application. Several stainless steels as well as 6Al–4V titanium do not appear to suffer from corrosion caused by ammonia–water.

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